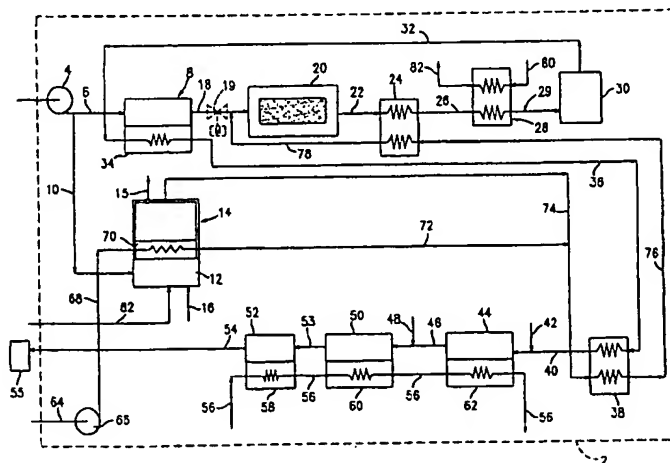




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(54) Title: SYSTEM FOR DESULFURIZING A FUEL FOR USE IN A FUEL CELL POWER PLANT



(57) Abstract

A fuel processing system is operable to remove substantially all of the sulfur present in an undiluted hydrocarbon fuel stock supply used to power a fuel cell power plant in a mobile environment, such as an automobile, bus, truck, boat, or the like, or in a stationary environment. The power plant hydrogen fuel source can be gasoline, diesel fuel, naphtha, light hydrocarbon fuels such as butane, propane, natural gas, or other like fuels which contain relatively high levels of organic sulfur compounds such as mercaptans, sulfides, disulfides, and the like. The undiluted hydrocarbon fuel supply is passed through a nickel desulfurizer bed wherein essentially all of the sulfur in the organic sulfur compounds react with the nickel reactant, and are converted to nickel sulfide while the desulfurized organic remnants continue through the remainder of the fuel processing system. The system does not require the addition of steam or a hydrogen source to the fuel stream prior to the desulfurizing step. The system operates at relatively low temperatures and can be used to desulfurize either a liquid or a gaseous fuel stream.

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Description

System for Desulfurizing a Fuel for Use in a Fuel Cell Power Plant

Technical Field

The present invention relates to an improved system for desulfurizing a raw hydrocarbon fuel stream so as to render the fuel suitable for use in a mobile vehicular fuel cell power plant assembly. More particularly, the desulfurizing system of this invention is operable to remove organic sulfur compounds found in the raw fuel stream to levels which will not poison the catalyst in the fuel processing section of the fuel cell power plant assembly.

Background of the Invention

Raw fuels, such as natural gas, gasoline, diesel fuel, naphtha, fuel oil, and like hydrocarbon fuels may not be useful as a process fuel source suitable for a fuel cell power plant due to the existence of relatively high levels of naturally-occurring complex organic sulfur compounds, or sulfur compounds added as odorants, such as mercaptans and thiophenes. Hydrogen generation in the presence of sulfur results in a poisoning effect on all of the catalysts used in the hydrogen generation system, often including the fuel cell anode catalyst. Conventional fuel processing systems used with stationary fuel cell power plants include a thermal steam reformer, such as that described in U.S. Patent No. 5,516,344. In such a fuel processing system, sulfur is removed by conventional hydrodesulfurization techniques which typically rely on a certain level of recycle as a source of hydrogen for the process. The recycle hydrogen combines with the organic sulfur compounds to form hydrogen sulfide within a catalytic

bed. The hydrogen sulfide is then removed using a zinc oxide bed to form zinc sulfide. The general hydrodesulfurization process is disclosed in detail in U.S. Patent No. 5,292,428. While this system is effective for use in large stationary applications, it does not readily lend itself to mobile transportation applications because of system size, cost and complexity. Additionally, the gas being treated must use process recycle in order to provide hydrogen in the gas stream, as noted above.

Other fuel processing systems, such as a conventional autothermal reformer, which use a higher operating temperature than conventional thermal steam reformers, can produce a hydrogen-rich gas in the presence of the foresaid complex organic sulfur compounds without prior desulfurization. When using an autothermal reformer to process raw fuels which contain complex organic sulfur compounds, the result is a loss of autothermal reformer catalyst effectiveness and useful catalyst life of the remainder of the fuel processing system. The organic sulfur compounds are converted to hydrogen sulfide as part of the reforming process. The hydrogen sulfide can then be removed using a solid absorbent scrubber, such as an iron or zinc oxide bed to form iron or zinc sulfide. The aforesaid solid scrubber systems are limited due to thermodynamic considerations, as to their ability to lower sulfur concentrations to non-catalyst degrading levels in processing components downstream of the reformer, such as in the shift converter, or the like.

Alternatively, the hydrogen sulfide can be removed from the gas stream by passing the gas stream through a liquid scrubber, such as sodium hydroxide, potassium hydroxide, or amines. Liquid scrubbers are large and heavy, and are therefore useful principally only in stationary fuel cell power plants. From the aforesaid, it is apparent that current methods for dealing with the presence of complex organic sulfur

compounds in a raw fuel stream for use in a fuel cell power plant require increasing fuel processing system complexity, volume and weight, and are therefore not suitable for use in mobile transportation systems.

An article published in connection with the 21st Annual Power Sources Conference proceedings of May 16-18, 1967, pages 21-26, entitled "Sulfur Removal for Hydrocarbon-Air Systems", and authored by H. J. Setzer et al, relates to the use of fuel cell power plants for a wide variety of military applications. The article describes the use of high nickel content hydrogenation catalyst to remove sulfur from a military fuel called JP-4, which is a jet engine fuel, and is similar to kerosene, so as to render the fuel useful as a hydrogen source for a fuel cell power plant. The systems described in the article operate at relatively high temperatures in the range of 600°F to 700°F. The article also indicates that the system tested was unable to desulfurize the raw fuel alone, without the addition of water or hydrogen, due to reactor carbon plugging. The carbon plugging occurred because the tendency for carbon formation greatly increases in the temperature range between about 550°F and about 750°F. A system operating in the 600°F to 700°F range, as disclosed in the article, would be very susceptible to carbon plugging, as was found to be the case in the system described in the article. The addition of either hydrogen or steam reduces the carbon formation tendency by supporting the formation of gaseous carbon compounds thereby limiting carbon deposits which cause the plugging problem.

It would be highly desirable from an environmental standpoint to be able to power electrically driven vehicles, such as an automobile, for example, by means of fuel cell-generated electricity; and to be able to use a fuel such as gasoline, diesel fuel,

naphtha, lighter hydrocarbon fuels such as butane, propane, natural gas, or like fuel stocks, as the fuel consumed by the vehicular fuel cell power plant in the production of electricity. In order to provide such a vehicular power source, the amount of sulfur in the processed fuel gas would have to be reduced to and maintained at less than about 0.05 parts per million.

Disclosure of the Invention

This invention relates to an undiluted fuel processing system which is operable to remove substantially all of the sulfur present in an undiluted hydrocarbon fuel stock used to power a fuel cell power plant in a mobile environment. The power plant fuel can be gasoline, diesel fuel, lighter hydrocarbon fuels, such as butane, propane, natural gas, or other similar fuels which contain relatively high levels of organic sulfur compounds such as thiophenes, mercaptans, sulfides, disulfides, and the like. The undiluted hydrocarbon fuel stock, without the use of steam or recycled gas streams, is first passed through a nickel desulfurizer bed wherein essentially all of the sulfur in the organic sulfur compounds react with the nickel reactant and are converted to nickel sulfide and desulfurized hydrocarbons which continue through the remainder of the fuel processing system. Since this desulfurizer requires no water or recycle addition, it can be made compact and simple when compared to alternate approaches, and it is not limited by thermodynamic considerations in the presence of water, as are other absorbents such as zinc or iron oxides. For example, zinc oxide, which is frequently used to remove hydrogen sulfide by the reaction:



cannot lower the H_2S sufficiently to protect the hydrogen generation catalyst in the presence of water vapor because the reaction is thermodynamically forced from right to left. Iron oxide, which is also frequently used to remove hydrogen sulfide is plagued

with the same limitation.

The desulfurized fuel is then passed in a vaporous state through a reformer, such as an autothermal reformer, for example, wherein the fuel is converted to a hydrogen-enriched fuel which is suitable for use in the anode side of the fuel cell assembly portion of the fuel cell power plant. The fuel may be desulfurized while in a gaseous state or in a liquid state. Steam for processing of the desulfurized fuel stream is provided by a steam generator. Heated ambient air and steam are used in the fuel gas reforming station. The reformed gas stream is passed through a shift converter which reduces the CO content and enriches the H₂ content of the gas stream; and thence through one or more stages of selective oxidizers which further reduce the CO content of the gas stream. The final processing step is an ammonia-removal step wherein ammonia is removed from the processed fuel stream prior to feeding the latter to the fuel cell assembly anodes. The fuel processing system may include a desulfurized fuel reservoir between the desulfurizer and the reformer so as to ensure that desulfurized fuel is available when the vehicle is restarted after shut-down.

It is therefore an object of this invention to provide a fuel processing system which is suitable for use in a mobile electrically-powered vehicle.

It is an additional object of this invention to provide a fuel processing system of the character described wherein a raw hydrocarbon fuel stock is desulfurized to an extent needed to produce a gaseous fuel cell power plant-compatible fuel stream.

It is a further object of this invention to provide a fuel processing system of the character described wherein the raw hydrocarbon fuel stock being desulfurized can be

gasoline, diesel fuel, naphtha and/or lighter hydrocarbon fuels such as butane, propane, natural gas, or the like.

It is another object of this invention to provide a fuel processing system of the character described wherein the raw hydrocarbon fuel stock is desulfurized by reacting the raw fuel with a nickel reactant bed, which bed is operative to convert sulfur compounds in the raw fuel to nickel sulfide which is deposited on the bed, with the desulfurized hydrocarbon fuel continuing through the fuel processing system.

It is a further object of this invention to provide a fuel processing system of the character described wherein the nickel bed can capture from 2-5% of its weight in sulfur when the sulfur compounds are thiophenes, and up to 15% of its weight in sulfur, when the sulfur compounds are mercaptans.

It is yet another object of this invention to provide a sulfur scrubber unit of a size, weight and complexity that is suitable for transportation applications and allows the subsequent fuel processing equipment to be kept to a size that is usable in transportation applications.

These and other objects of the invention will become more readily apparent from the following detailed description thereof when taken in conjunction with the accompanying drawings in which:

Brief Description of the Drawings

Fig. 1 is a schematic view of a first embodiment of a fuel processing system which is formed in accordance with this invention;

Fig. 2 is a schematic view of a second embodiment of a fuel processing system which is formed in accordance with this invention;

Fig. 3 is a schematic view of a third embodiment of a fuel processing system which is formed in accordance with this invention;

Fig. 4 is a fragmented schematic view of a portion of a fuel processing system which is formed in accordance with this invention and which provides a reserve desulfurized fuel supply for start-up of the system;

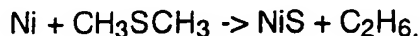
Fig. 5 is a fragmented schematic view of a portion of a fuel processing system similar to FIG. 4 but which illustrates an alternative configuration of the system for providing a reserve desulfurized fuel supply for start-up of the system; and

Fig. 6 is a schematic perspective view of an automobile which is equipped with an electric motor for providing power for the automobile, and a fuel cell assembly for supplying electricity to the electric motor.

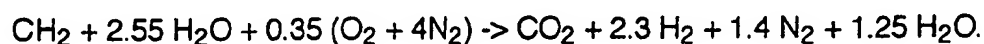
Specific Modes for Carrying Out the Invention

Referring now to the drawings, Fig. 1 is a schematic view of a fuel processing system, denoted generally by the numeral 2, which is suitable for use in a vehicle such as an automobile. The fuel being processed, as noted above, can be gasoline. A fuel pump 4 pumps the gasoline into the system 2 via line 6 which leads to a nickel desulfurizer bed 8. A branch line 10 is provided to bleed off a portion of the gasoline to feed a burner 12 in a boiler 14 which produces steam for the fuel processor system 2. The

boiler 14 contains water which is converted to steam in the boiler 14. Air enters the burner 12 through line 16. The burner exhaust is flushed from the system 2 via an exhaust line 15. Organic sulfur compounds in the gasoline are broken down by the nickel reactant per the following typical reactions:



The desulfurizer 8 operates at a pressure of between ambient and about one hundred fifty psi, and a temperature of between about 200°F and 525°F so that gasoline entering the desulfurizer 8 at a temperature of about 75°F (ambient) will be preheated and vaporized in the desulfurizer 8. The temperature of the desulfurized gasoline will be raised to about 375°F when the vaporized fuel enters a passage 18 which leads to an autothermal reformer 20. The reformer 20 may be provided with an iron oxide catalyst section as described in U.S. Patent No. 4,451,578, which is incorporated herein in its entirety. Overall, the desulfurized gasoline vapor fuel gas is converted to a hydrogen-enriched fuel gas per the following representative reaction which includes a complete shift of CO to CO₂:



Within the reformer 20, the fuel gas reaches a thermodynamic equilibrium at 1,200°F which produces approximately equal quantities of CO and CO₂ and a trace of methane. The reformer 20 operates at an inlet temperature of about 950°F where a portion of the fuel gas stream is combusted and the remainder reformed to an H₂-enriched gas stream, so that the reformed gas stream enters a line 22 at a temperature of about 1,200°F. The hydrogen-enriched fuel gas passes from the line 22 into a heat exchanger 24 wherein the temperature of the fuel gas is lowered to about 760°F. The

cooled gas stream passes from the heat exchanger 24 through a line 26 to a burner fuel preheater 28 wherein the temperature of the fuel gas stream is lowered to about 400°F. The cooled fuel gas stream then flows through a line 29 to a shift converter 30 wherein the CO content of the gas stream is reduced to an amount in the range of about 0.5% to about 1.0% by means of the following reaction:

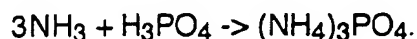


and wherein the gas stream temperature increases to about 525°F. The treated gas stream then flows through a line 32 and through a heat exchanger 34 which controls the temperature in the desulfurizer 8. The gas stream is cooled to a temperature of about 425°F in the heat exchanger 34 and then flows through a line 36 to a heat exchanger 38 wherein the temperature of the fuel gas stream is lowered to about 350°F. The cooled gas stream then flows through a line 40 wherein it is admixed with air introduced into the line 40 via an air inlet line 42. The amount of oxygen in the line 42 is about 1.0% of the total gas flow. The oxygenated fuel gas stream then flows through a first selective oxidizer 44 wherein the gas stream is cooled to a temperature of about 300°F and wherein CO is removed from the gas stream via the reaction:



The cooled and treated fuel gas stream then flows through a line 46 wherein it is again admixed with air introduced into the line 46 via an air inlet line 48. The amount of oxygen in the line 48 is about 0.35% of the total gas flow or less. The oxygenated fuel gas stream then passes through a second selective oxidizer 50 wherein the temperature of the fuel gas stream is lowered to about 170°F and the CO content is reduced to less than 10 ppm by volume. The cooled gas stream then passes through a line 53 to an ammonia scrubber 52 which may be a phosphoric acid-impregnated carbon bed. An example of the aforesaid procedure is described in U.S. Patent No.

4,379,036. In some circumstances, a single stage selective oxidizer using additional air and cooling, and operating in the 170°F range could be used. At a temperature of about 170°F the ammonia is removed from the gas stream in the scrubber 52 via the reaction:



Alternatively, the ammonia can be dissolved in water or reacted with the acid in an acidic polymer, such as Nafion®, to an ammonium salt such as $(\text{NH}_4)_2\text{SO}_4$. The fully treated fuel gas stream then flows through a line 54 to the anode side of a fuel cell stack assembly 55 of the fuel cell power plant where it serves as the reactant fuel for the electrochemical reaction which proceeds in the power section of the power plant.

The temperatures of the ammonia scrubber 52 and the selective oxidizers 50 and 44 are controlled by the vehicle coolant which flows through lines 56 and through heat exchangers 58, 60 and 62 which are associated with the ammonia scrubber 52 and the selective oxidizers 50 and 44 respectively. The vehicle coolant flows through the heat exchangers 58, 60 and 62 in counter direction to the gas stream so that the temperature of the coolant fluid will increase from about 160°F at its inlet to about 270°F at its outlet.

Autothermal reformer process air enters the system 2 via line 64 wherein it is pressurized by means of a pump 66. Air entering the system 2 is at ambient temperature of about 75°F. The air stream passes through a line 68 to a heat exchanger 70 in the boiler 14 wherein the temperature of the air stream is raised to about 225°F. The heated air passes from the heat exchanger 70 into a line 72 and

flows thence to a second line 74 where it admixes with steam emanating from the boiler 14. The air-steam admixture then flows through the heat exchanger 38 wherein the temperature of the air-steam admixture is raised to about 330°F. The heated air-steam admixture then flows through a line 76, through the heat exchanger 24 where the temperature of the air-steam admixture is raised to about 950°F. The heated air-steam admixture then flows through the line 78 and into the line 18 wherein mixture of the gasoline fuel vapor and the air-steam admixture occurs. The fuel-air-steam mixture then enters the reformer 20.

Anode exhaust, which is used as an energy source, enters the burner fuel preheater 28 via line 80 at a temperature of about 120°F. The anode exhaust stream is heated to a temperature of about 700°F in the preheater 28. The heated anode exhaust stream then flows through a line 82 to the burner 12 wherein it admixes with the air and gasoline.

The aforesaid system 2 is designed to process a vaporized fuel supply in the desulfurizer 8. The system 2 can also process a liquid fuel supply in the desulfurizer 8. When a liquid fuel supply is processed, a pressurization valve 19 (shown in phantom) will be positioned in the line 18 so as to ensure that the fuel can remain in a liquid state at the high operating temperatures of the desulfurizer 8 which may be pressurized up to about 150 psig by the fuel pump 4.

When a large increase in power is requested, the valve 19 downstream of the desulfurizer 8 can be opened to provide a high fuel flow rate. Most of the liquid fuel at the valve inlet will flash evaporate as it goes through the valve, with the remainder

being evaporated by the steam, thereby providing a rapid response of gaseous fuel to the reformer 20.

Referring now to FIG. 2, an alternative embodiment of the system 2 is depicted. Instead of using a boiler fueled by the fuel stock to produce the steam needed in the reformer, the system uses a first steam generator sub-assembly 84 which receives water from a line 86 and uses the heat exchangers 58, 60 and 62 to convert the water in the line 86 to steam, which steam exits the heat exchanger 62 through line 88. Ambient air is admitted to the system 2 through line 64 and pump 66 and is directed through line 90 to the line 88 wherein the air mixes with the steam in line 88. The pre-shift converter heat exchanger 28 is used as a second steam generator by passing a water stream through a line 92 through the heat exchanger 28. Steam exits from the heat exchanger 28 through line 94 and combines with the air and steam in the line 88. The combined stream then flows through the line 78 to the pre-reformer line 18, and the processing proceeds as previously described.

Referring now to FIG. 3, yet another embodiment of the system 2 is depicted. In the embodiment of FIG. 3, the ammonia scrubber 52 takes the form of a water absorbent wherein ammonia in the fuel gas stream is dissolved in water in the scrubber 52 by means of a contact cooler as generally described in U.S. Patent No. 4,816,040. The water is admitted to the scrubber 52 through a line 96, and water with dissolved ammonia is removed from the scrubber 52 via line 98 and admitted into the boiler 14 wherein the ammonia comes to an equilibrium state in the water. Use of the aforesaid device provides the ability to control the anode gas feed temperature and gas dew point. The remainder of the system 2 operates essentially as described in connection with FIG. 1.

Referring now to FIGS. 4 and 5, there are shown two variations of a portion of the system 2 wherein a reserve supply of desulfurized fuel is provided so as to enable the vehicle to be readily restarted after shut down of a previous operating cycle. The restart supply of desulfurized fuel is drawn off into a restart fuel tank 100 during an operating cycle of the system 2. The start up desulfurized reserve fuel supply is maintained in a liquid form in the tank 100. In both variations, the valve 19 is employed in the line 18 to maintain the liquid phase of the fuel in the tank 100, and the liquid desulfurized fuel reserve is drawn into the tank 100 through a branch line 102 which communicates with the line 18 upstream of the valve 19.

In the embodiment shown in FIG. 4, a pump 104 is provided adjacent to the tank 100 and is operative on start up to draw the desulfurized fuel from the tank 100 and pumps the fuel through a line 106 and a selectively opened valve 107 back up to the line 18 downstream of the valve 19 where the desulfurized fuel enters the reformer 20.

In the embodiment shown in FIG. 5, the pump 4 is used to draw the desulfurized fuel from the tank 100 through a line 106 after a valve 21 is opened. The pump 4 then pumps the fuel back through the desulfurizer 8, through the valve 19 and into the reformer 20.

FIG. 6 is a schematic illustration of an automobile, denoted generally by the numeral 110, which has been modified so as to operate with the fuel cell power plant electricity source-and-fuel-processing assembly of this invention. The automobile 110 is powered by an electric motor 112 which drives a trans-axle 114. The embodiment of the automobile 110 shown in the drawing utilizes a bi-modal source of electricity for

the electric motor 112, which electricity source includes the fuel cell power plant assembly 116, and an additional source of electricity 122 which can be a storage battery, a gas-powered generator, or the like. A start-up battery 127 can also be included in the automobile to start up the components of the power system 2. It will be appreciated that the automobile 110 could utilize only the fuel cell power plant assembly 116 to provide electricity for the electric motor 112. The automobile 110 includes a fuel tank 118 having a line 120 which leads to the fuel processing assembly 2. FIG. 6 shows a layout plan for the fuel processing assembly 2, the boiler 14, the ammonia scrubber 52, the cell stack 55, and a coolant system 124 and a water demineralizer 126.

It will be readily appreciated that by using an initial nickel desulfurizer, the amount of sulfur in the processed fuel stream can be lowered to less than about 0.05 parts per million, a level which will not significantly affect the catalyst beds in the reformer, selective oxidizer, and shift converter or in the active section of the fuel cell assembly. As a result, fuels which possess relatively large percentages of organic sulfur compounds such as gasoline, diesel fuel, lighter hydrocarbon fuels such as butane, propane, and natural gas, or the like fuel stocks, can thus be safely used for extended periods of time as the hydrocarbon fuel gas reactant in a fuel cell power plant that produces electricity to operate the vehicle. It will be appreciated that the system of this invention can be used as the sole source of electricity for a vehicle or a stationary power plant, or could be used in a hybrid system which could also include batteries for electrical power or generators for electrical power in addition to the fuel cell electrical power source.

Since many changes and variations of the disclosed embodiment of the invention may

be made without departing from the inventive concept, it is not intended to limit the invention otherwise than as required by the appended claims.

What is claimed is:

Claims

1. A system for desulfurizing an undiluted hydrocarbon fuel stream so as to convert the hydrocarbon fuel stream into a hydrogen-rich gas, which gas is suitable for use in a cell stack assembly in a fuel cell power plant, said system comprising:
 - a) a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
 - b) means for introducing the undiluted hydrocarbon fuel stream into said nickel desulfurization station; and
 - c) means for maintaining said nickel desulfurization station at an operating temperature in the range of about 250°F to about 525°F during operation of said system.
2. The system of Claim 1 wherein the fuel stream is gasoline, naphtha, diesel fuel or a light hydrocarbon fuel which is maintained in a liquid state in the nickel desulfurization station.
3. The system of Claim 2 further comprising means for pressurizing the nickel desulfurization station to a pressure which will ensure the liquid state of the fuel stream.
4. The system of Claim 3 wherein the nickel desulfurization station operates at a pressure from ambient pressure to about one hundred fifty psi.
5. The system of Claim 1 wherein the fuel stream is gasoline or diesel fuel which is maintained in a vaporous state in the nickel desulfurization station.
6. The system of Claim 1 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline; diesel fuel; naphtha; and light hydrocarbon fuels which are gaseous at ambient pressure.

7. The system of Claim 1 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline, diesel fuel, naphtha, butane, propane and natural gas.
8. The system of Claim 1 further comprising an autothermal reformer station; means for generating steam; and means for supplying air, whereby the autothermal reformer station receives a mixture of desulfurized fuel from said nickel desulfurization station, steam from said means for generating steam, and air from means for supplying air, and utilizes the fuel, steam and air mixture to produce a hydrogen rich gas stream.
9. The system of Claim 8 further comprising a shift converter station for receiving and processing the hydrogen rich gas stream from the autothermal reformer station.
10. The system of Claim 9 further comprising a selective oxidizer station for receiving and processing output from said shift converter station.
11. The system of Claim 9 wherein output from said shift converter station is a hydrogen rich gas having a CO content in the range of about 0.5% to about 1.0%.
12. The system of Claim 10 further comprising an ammonia scrubber station for receiving and processing output from said selective oxidizer station.
13. The system of Claim 12 wherein said ammonia scrubber station is a contact cooler.
14. The system of Claim 10 wherein said means for generating steam is a boiler heated by a combination of fuel cell anode exhaust and unprocessed fuel from said fuel stream.
15. The system of Claim 10 wherein said means for generating steam is a boiler heated by fuel cell anode exhaust.
16. The system of Claim 10 wherein said means for generating steam includes heat exchange components downstream of said autothermal reformer station.

17. The system of Claim 10 wherein said selective oxidizer station includes at least two beds, a first of which operates at a temperature of about 300°F and a second of which operates at a temperature of about 170°F, and wherein the hydrogen rich gas exiting said selective oxidizer has a CO content below about ten ppm.
18. The system of Claim 10 wherein said selective oxidizer station includes a single bed which operates at a temperature of about 170°F and wherein the hydrogen rich gas exiting the selective oxidizer has a CO content of less than about ten ppm.
19. The system of Claim 8 wherein said autothermal reformer station includes at least two catalyst beds, one comprising an iron oxide catalyst deposited on lanthanum-stabilized alumina; and another comprising a nickel catalyst deposited on lanthanum-stabilized alumina.
20. The system of Claim 1 further comprising a steam boiler station for producing steam for operating an autothermal reformer in said system.
21. The system of Claim 20 wherein said steam boiler station is fired by a diverted portion of said undiluted fuel stream.
22. The system of Claim 20 wherein steam boiler station is heated by fuel cell anode exhaust.
23. The system of Claim 20 further comprising means for delivering a supply of combustion air to said steam boiler station.
24. The system of Claim 20 further comprising means for delivering anode exhaust to said steam boiler station.
25. The system of Claim 11 further comprising heat exchanger means interposed between said autothermal reformer and a cell stack assembly for bringing the hydrogen-rich gas to a temperature of about 170°F prior to entering the cell stack

assembly.

26. The system of Claim 12 further comprising means for removing ammonia from the hydrogen-rich gas prior to the latter entering the cell stack assembly.

27. A method for desulfurizing an undiluted hydrocarbon fuel stream so as to convert the hydrocarbon fuel stream into a hydrogen-rich gas, which hydrogen-rich gas is suitable for use in a cell stack assembly in a fuel cell power plant, said method comprising the steps of:

- a) providing an undiluted hydrocarbon fuel stream;
- b) providing a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds in the hydrocarbon fuel stream to nickel sulfide;
- c) introducing the hydrocarbon fuel stream into said nickel desulfurization station; and
- d) maintaining said nickel desulfurization station at operating temperatures in the range of about 250°F to about 525°F during performance of the method.

28. The method of Claim 27 wherein said hydrocarbon fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline, diesel fuel, naphtha, and light hydrocarbon fuels which are gaseous at ambient pressure such as natural gas, propane, and like fuels.

29. The method of Claim 27 further comprising the step of pressurizing said nickel desulfurization station so as to preserve said hydrocarbon fuel stream in a liquid state.

30. The method of Claim 29 wherein said hydrocarbon fuel stream is gasoline.

31. The method of Claim 29 wherein said hydrocarbon fuel stream is diesel fuel.

32. The method of Claim 27 further comprising the step of providing a supply of steam for operating an autothermal reformer for performing the method.

33. A method for treating a hydrocarbon fuel stream, said method comprising:

- a) the step of providing an undiluted hydrocarbon fuel stream;
- b) the step of providing a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds in the hydrocarbon fuel stream to nickel sulfide;
- c) the step of introducing the hydrocarbon fuel stream into said nickel desulfurization station; and
- d) the step of maintaining said nickel desulfurization station at operating temperatures in the range of about 250°F to about 525°F during performance of the method.

34. A mobile wheeled land vehicle assemblage comprising:

- a) an onboard electric motor for providing at least partial motive power for the vehicle assemblage;
- b) an onboard fuel cell stack assembly for providing at least a portion of electricity for operating the electric motor; and
- c) an onboard fuel processing system for desulfurizing an undiluted hydrocarbon fuel stream so as to convert the hydrocarbon fuel stream into a hydrogen-rich gas, which hydrogen-rich gas is suitable for use in the cell stack assembly, said fuel processing system comprising:
 - i) a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds found in the fuel stream to nickel sulfide;
 - ii) means for introducing the undiluted hydrocarbon fuel stream into said nickel desulfurization station; and
 - ii) means for maintaining said nickel desulfurization station at an operating temperature in the range of about 250°F to about 525°F during operation of said system.

35. An assemblage for generating electricity from an undiluted hydrocarbon fuel stream, said assemblage comprising:

- a) a fuel cell stack assembly;
- b) a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;

- c) means for introducing the undiluted hydrocarbon fuel stream into said nickel desulfurization station; and
- d) means for maintaining said nickel desulfurization station at an operating temperature in the range of about 250°F to about 525°F during operation of said assemblage.

36. The assemblage of Claim 35 wherein the fuel stream is gasoline, naphtha, or diesel fuel which is maintained in a liquid state in the nickel desulfurization station.

37. The assemblage of Claim 36 further comprising means for pressurizing the nickel desulfurization station to a pressure which will ensure the liquid state of the fuel stream.

38. The assemblage of Claim 37 wherein the nickel desulfurization station operates at a pressure from ambient pressure to about one hundred fifty psi.

39. The assemblage of Claim 35 wherein the fuel stream is gasoline, naphtha or diesel fuel which is maintained in a vaporous state in the nickel desulfurization station.

40. The assemblage of Claim 35 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline; diesel fuel; naphtha; and light hydrocarbon fuels which are gaseous at ambient pressure.

41. The assemblage of Claim 35 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline, naphtha, diesel fuel, butane, propane and natural gas.

42. The assemblage of Claim 35 further comprising an autothermal reformer station; means for generating steam; and means for supplying air, whereby the autothermal reformer station receives a mixture of desulfurized fuel from said nickel desulfurization station, steam from said means for generating steam, and air from means for supplying air, and utilizes the fuel, steam and air mixture to produce a hydrogen rich gas stream.

43. The assemblage of Claim 42 further comprising a shift converter station for receiving and processing the hydrogen rich gas stream from the autothermal reformer station.
44. The assemblage of Claim 43 further comprising a selective oxidizer station for receiving and processing output from said shift converter station.
45. The assemblage of Claim 43 wherein output from said shift converter station is a hydrogen rich gas having a CO content in the range of about 0.5% to about 1.0%.
46. The assemblage of Claim 44 further comprising an ammonia scrubber station for receiving and processing output from said selective oxidizer station.
47. The assemblage of Claim 46 wherein said ammonia scrubber station is a contact cooler.
48. The assemblage of Claim 44 wherein said means for generating steam is a boiler heated by a combination of fuel cell anode exhaust and unprocessed fuel from said fuel stream, or by fuel cell anode exhaust alone.
49. The assemblage of Claim 44 wherein said means for generating steam includes heat exchange components downstream of said autothermal reformer station.
50. The assemblage of Claim 44 wherein said selective oxidizer station includes at least two beds, a first of which operates at a temperature range of about 300°F and a second of which operates at a temperature of about 170°F, and wherein the hydrogen rich gas has a CO content below about ten ppm.
51. The assemblage of Claim 44 wherein said selective oxidizer station includes a single bed which operates at a temperature of about 170°F, and wherein the hydrogen rich gas has a CO content below about ten ppm.
52. The assemblage of Claim 42 wherein said autothermal reformer station includes

at least two reactant beds, one comprising an iron oxide reactant deposited on lanthanum-stabilized alumina; and another comprising a nickel reactant deposited on lanthanum-stabilized alumina.

53. The assemblage of Claim 35 further comprising a steam boiler station for producing steam for operating an autothermal reformer in said system.

54. The assemblage of Claim 53 wherein said steam boiler station is fired by a diverted portion of said undiluted fuel stream.

55. The assemblage of Claim 53 further comprising means for delivering a supply of combustion air to said steam boiler station.

56. The assemblage of Claim 53 further comprising means for delivering anode exhaust to said steam boiler station.

57. The assemblage of Claim 45 further comprising heat exchanger means interposed between said autothermal reformer and a cell stack assembly for bringing the hydrogen-rich gas to a temperature of about 170°F prior to entering said cell stack assembly.

58. The assemblage of Claim 35 wherein said cell stack assembly includes proton exchange membrane electrolytes.

59. A mobile wheeled land vehicle assemblage which is powered by an electric motor, said assemblage comprising:

- a) a fuel cell stack assembly;
- b) a nickel desulfurization station containing a nickel reactant which is operative to convert sulfur contained in organic sulfur compounds contained in the fuel stream to nickel sulfide;
- c) means for introducing the undiluted hydrocarbon fuel stream into said nickel desulfurization station; and
- d) means for maintaining said nickel desulfurization station at an operating

temperature in the range of about 250°F to about 525°F during operation of said assemblage.

60. The assemblage of Claim 59 wherein the fuel stream is gasoline, naphtha or diesel fuel which is maintained in a liquid state in the nickel desulfurization station.

61. The assemblage of Claim 60 further comprising means for pressurizing the nickel desulfurization station to a pressure which will ensure the liquid state of the fuel stream.

62. The assemblage of Claim 61 wherein the nickel desulfurization station operates at a pressure from ambient pressure to about one hundred fifty psi.

63. The assemblage of Claim 59 wherein the fuel stream is gasoline, naphtha or diesel fuel which is maintained in a vaporous state in the nickel desulfurization station.

64. The assemblage of Claim 59 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline; diesel fuel; naphtha; and light hydrocarbon fuels which are gaseous at ambient pressure.

65. The assemblage of Claim 59 wherein the fuel stream is a hydrocarbon fuel selected from the group consisting of gasoline, diesel fuel, butane, propane and natural gas.

66. The assemblage of Claim 59 further comprising an autothermal reformer station; means for generating steam; and means for supplying air, whereby the autothermal reformer station receives a mixture of desulfurized fuel from said nickel desulfurization station, steam from said means for generating steam, and air from means for supplying air, and utilizes the fuel, steam and air mixture to produce a hydrogen rich gas stream.

67. The assemblage of Claim 66 further comprising a shift converter station for receiving and processing the hydrogen rich gas stream from the autothermal reformer station.

68. The assemblage of Claim 67 further comprising a selective oxidizer station for receiving and processing output from said shift converter station.

69. The assemblage of Claim 67 wherein output from said shift converter station is a hydrogen rich gas having a CO content in the range of about 0.5% to about 1.0%.

70. The assemblage of Claim 68 further comprising an ammonia scrubber station for receiving and processing output from said selective oxidizer station.

71. The assemblage of Claim 70 wherein said ammonia scrubber station is a contact cooler.

72. The assemblage of Claim 68 wherein said means for generating steam is a boiler heated by a combination of fuel cell anode exhaust and unprocessed fuel from said fuel stream.

73. The assemblage of Claim 68 wherein said means for generating steam includes heat exchange components downstream of said autothermal reformer station.

74. The assemblage of Claim 68 wherein said selective oxidizer station includes at least two beds, a first of which operates in a temperature range of about 300°F and a second of which operates in a temperature of about 170°F and wherein the hydrogen rich gas has a CO content below about ten ppm.

75. The assemblage of Claim 68 wherein said selective oxidizer station includes a single bed which operates in a temperature of about 170°F and wherein the hydrogen rich gas has a CO content below about ten ppm.

76. The assemblage of Claim 62 wherein said autothermal reformer station includes at least two catalyst beds, one comprising an iron oxide catalyst deposited on lanthanum-stabilized alumina; and another comprising a nickel catalyst deposited on lanthanum-stabilized alumina.

77. The assemblage of Claim 59 further comprising a steam boiler station for producing steam for operating an autothermal reformer in said system.
78. The assemblage of Claim 72 wherein said steam boiler station is fired by a diverted portion of said undiluted fuel stream.
79. The assemblage of Claim 72 further comprising means for delivering a supply of combustion air to said steam boiler station.
80. The assemblage of Claim 72 further comprising means for delivering anode exhaust to said steam boiler station.
81. The assemblage of Claim 68 further comprising heat exchanger means interposed between said autothermal reformer and a cell stack assembly for bringing the hydrogen-rich gas to a temperature of about 170°F prior to entering said cell stack assembly.
82. The assemblage of Claim 59 wherein said cell stack assembly includes at least one proton exchange membrane electrolyte.

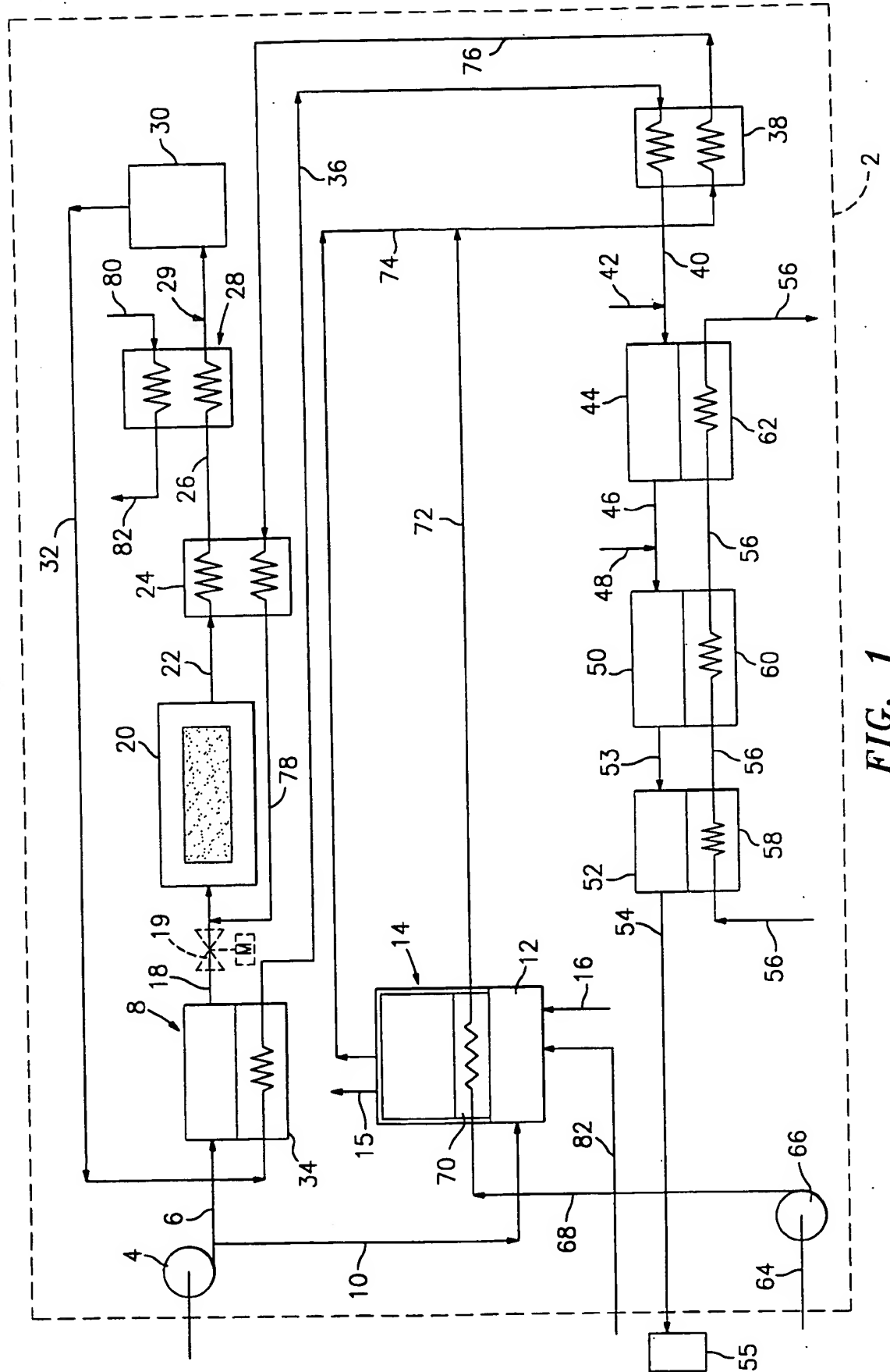


FIG. 1

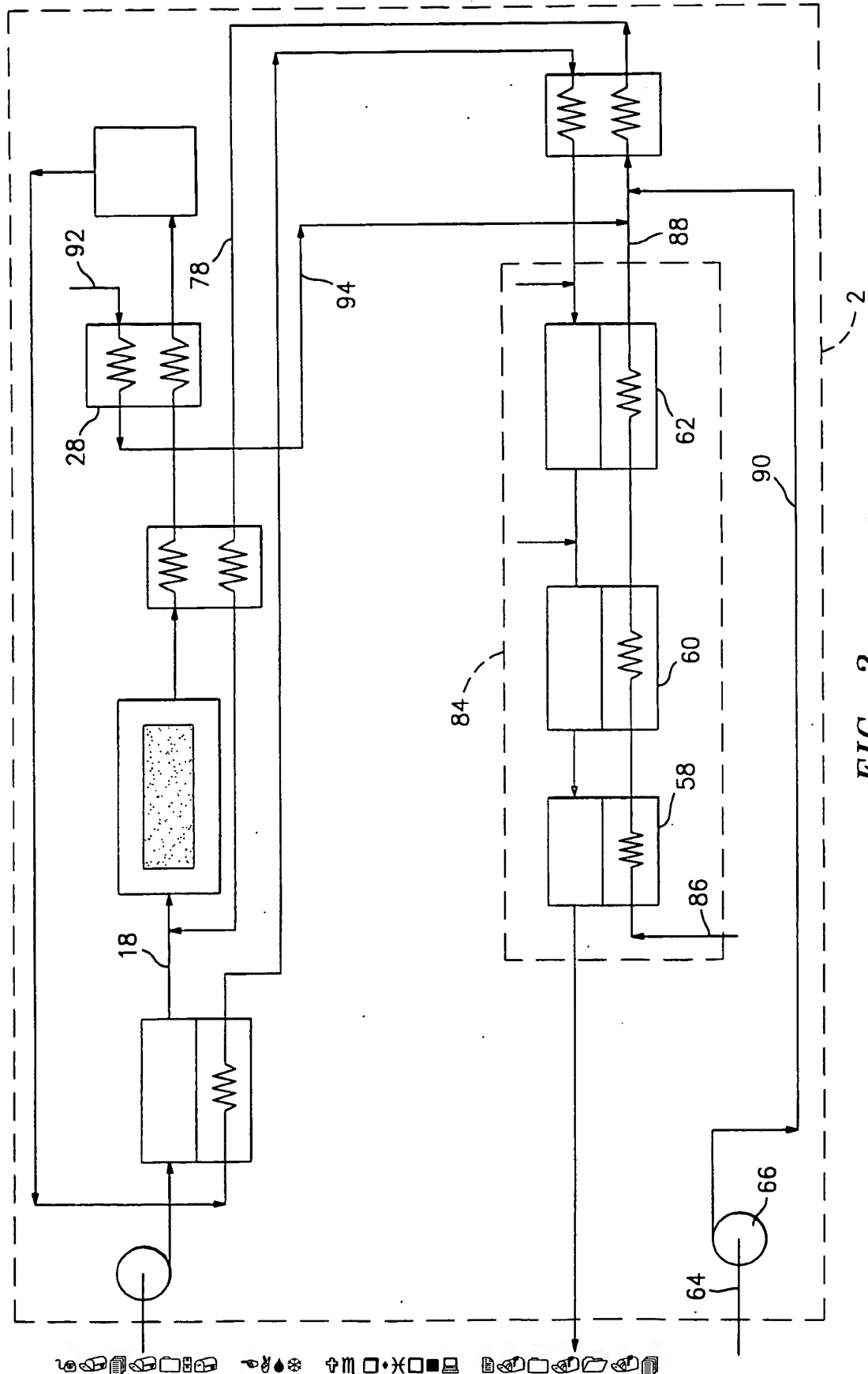


FIG. 2

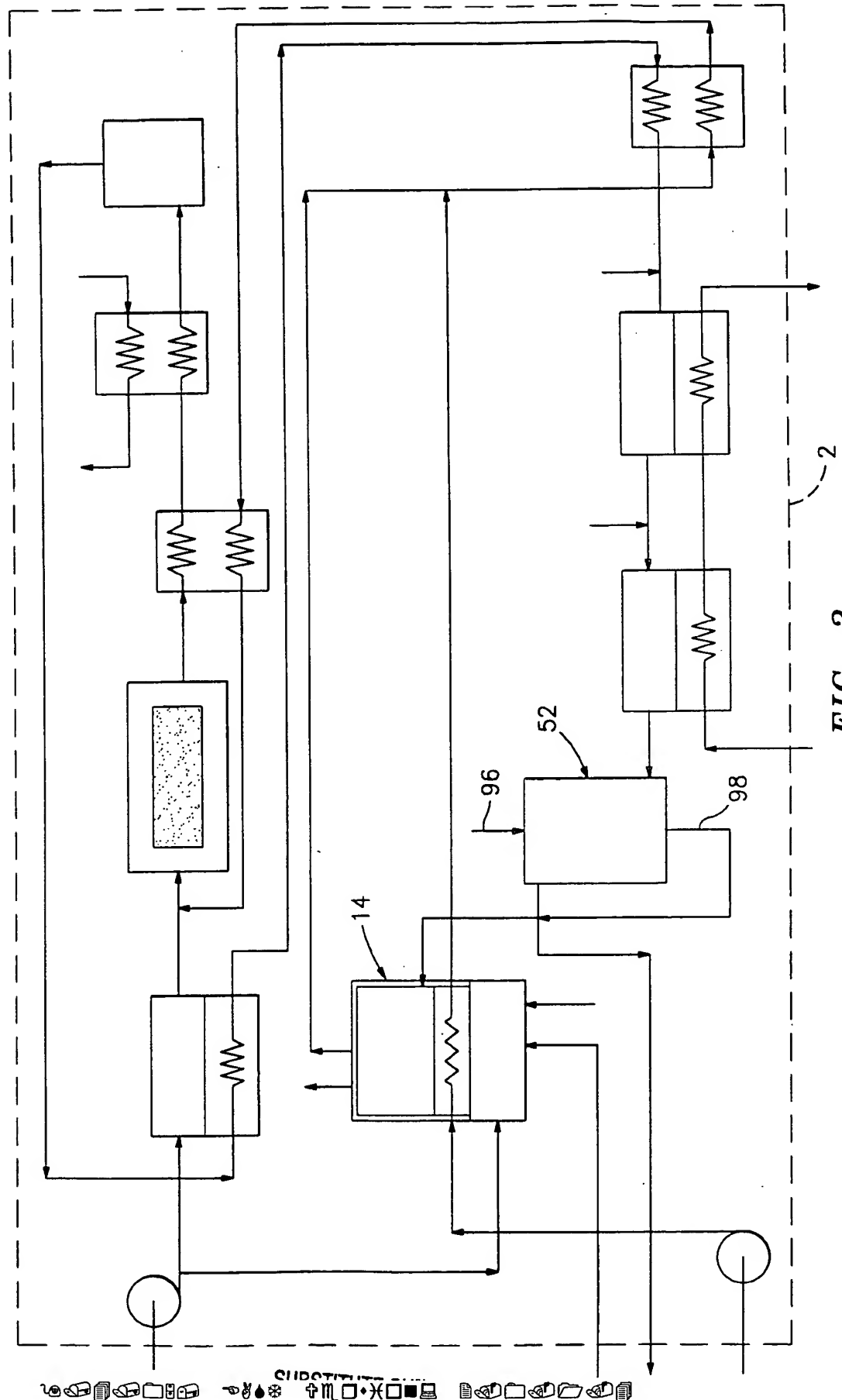


FIG. 3

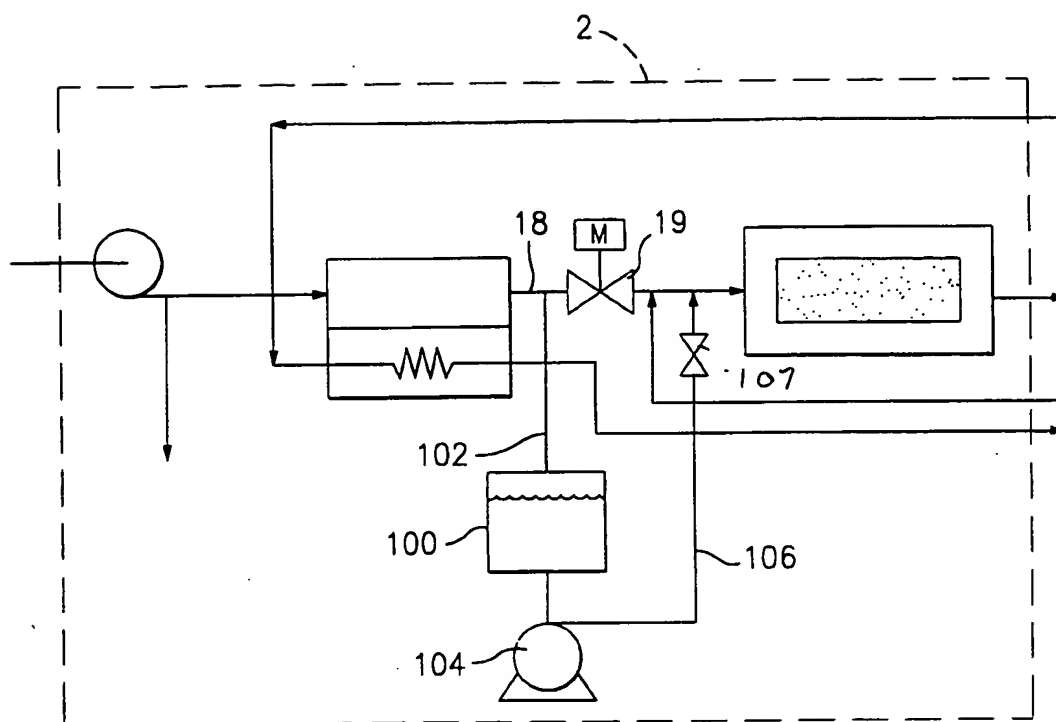


FIG. 4

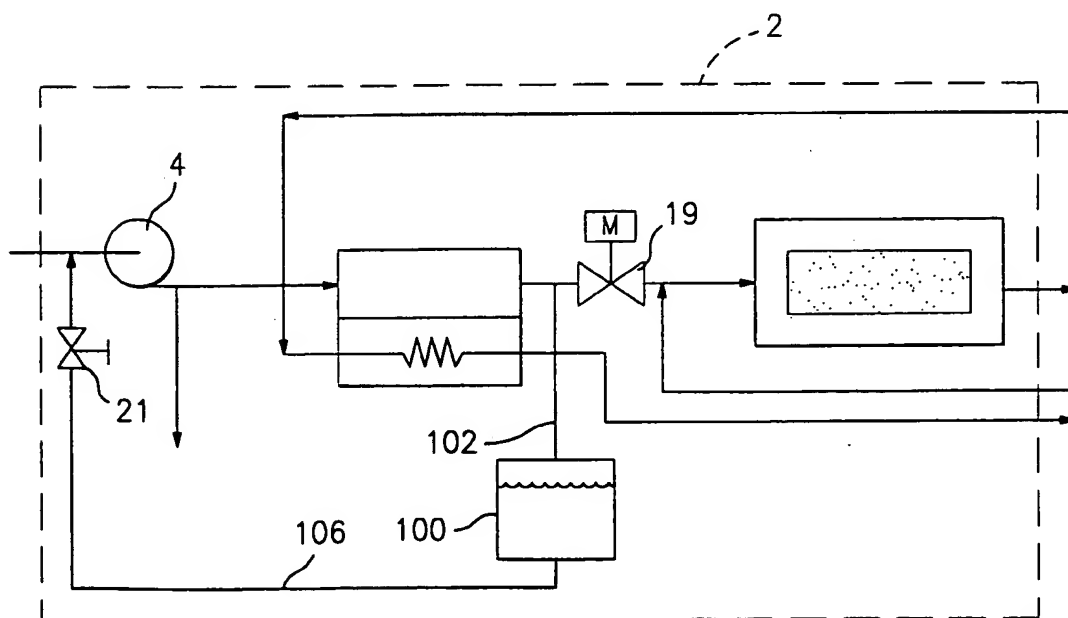


FIG. 5

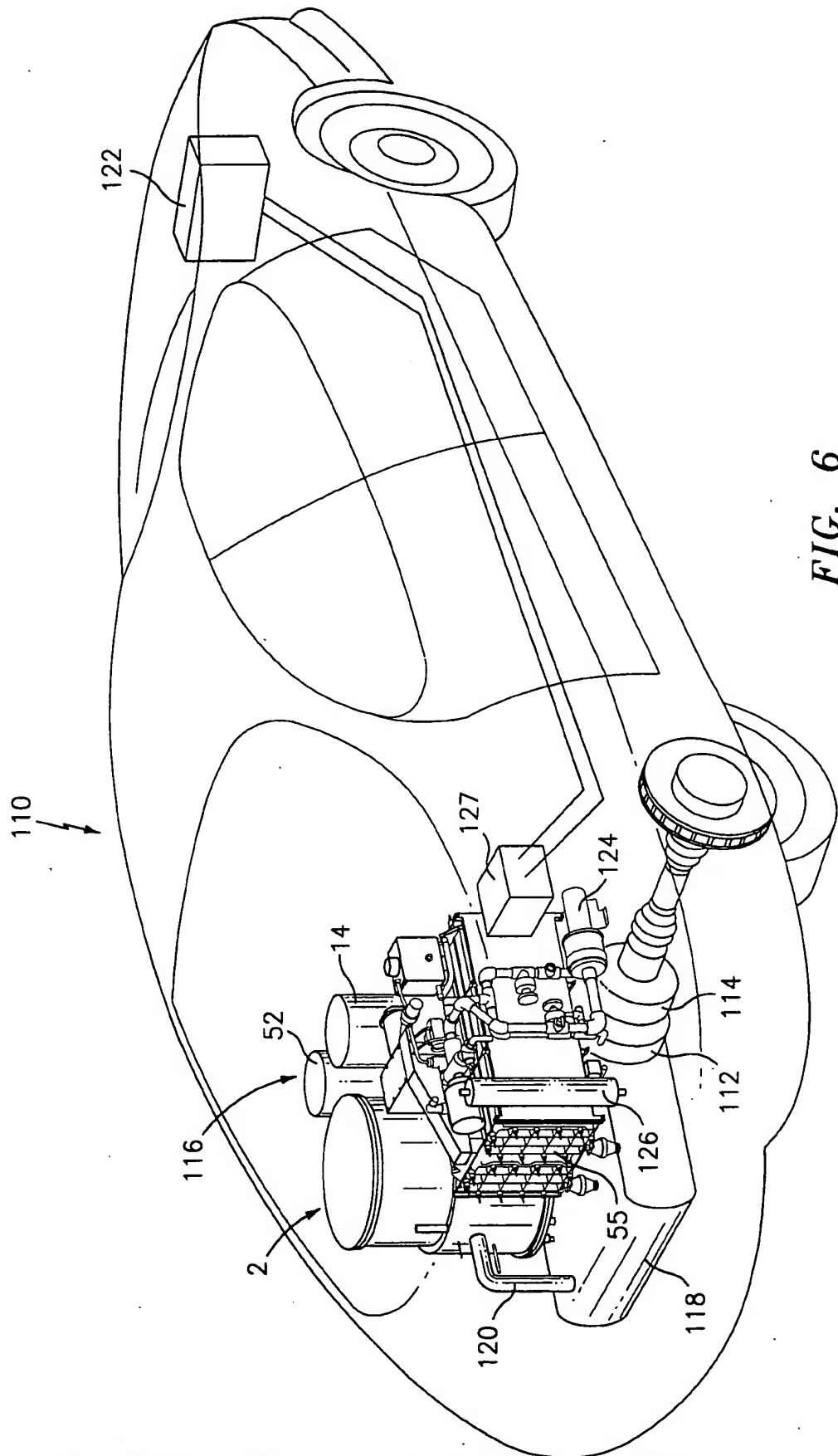


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/14319

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 7/00; C01F 17/32

US CL : 48/61; 423/561.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 48/61; 422/177, 198, 211; 423/245.1, 245.3, 561.1; 429/13,17,19,20.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,273,748 A (TAKAHASHI et al.) 16 June 1981, Abstract, cloumn 2 lines 24-36, Figure 4, column 1 lines 7-25, claims 17, 19 and 25, column 10 lines 9-10.	1-33
Y	US 4,816,040 A (BONVILLE et al.) 28 March 1989, Abstract, column 1 lines 39-50.	13
Y	US 5,026,536 A (SHIORI et al.) 25 June 1991, column 3 line 8, column 3 line 67, column 4 line 5, column 4 line 19.	19
Y	US 5,271,916 A (VANDERBORGH et al.) 21 December 1993, Abstract.	10, 12-17
Y	US 5,686,196 A (SINGH) 11 November 1997, Figure, Abstract, column 3 line 1.	2-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 AUGUST 1999

Date of mailing of the international search report

28 OCT 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/14319

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,747,185 A (HSU) 05 May 1998, column 1 lines 55-58, column 2 line 29, column 3 lines 4-5, column 3 37-51, column 3 line 65-67, column 8 lines 50-65.	8, 14, 15, 16, 21, 22, 25.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/14319

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-33

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

International application No.
PCT/US99/14319

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-33, drawn to the system and method for desulfurizing a hydrocarbon fuel stream .

Group II, claims 34 and 59-82, drawn to a vehicle.

Group III, claims 35-58, drawn to an assemblage for generating electricity.

The inventions listed as Groups I, II, and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: group I, the system and method for desulfurization does not contain the group II vehicle components, or the group III assemblage claims. Group II does not contain group III claims drawn to an assemblage for generating electricity.

